Review

In-situ catalytic abatement of NO_x during fluidized bed combustion—A literature study

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Abstract

In this study, opportunities, challenges, and possibilities to develop a bed material for in-situ catalytic reduction of NO_x during fluidized bed combustion have been identified. Various catalytic materials and processes for abatement of NO_x at high temperatures are reviewed, which include De-NO_x catalysis, catalytic decomposition, and selective catalytic oxidation of NO_x precursors in combustion processes. Possibilities to utilize fly ash from combustion itself for the development are discussed.
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Contents

1. Nitrogen oxides and NO_x abatement techniques for stationary sources

Nitrogen oxides (NO_x), collectively referred to nitric oxide (NO) and nitrogen dioxide (NO_2), are emitted primarily from combustion processes. In the normal conditions of atmospheric

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pressure and 25 °C, nitric oxide is a colourless and odourless gas, while nitrogen dioxide is a pungent reddish-brown gas. They are both noxious and directly responsible for large contributions to the formation of acid rain and resultant acidification, ground-level atmospheric ozone (photochemical smog), and general atmospheric visibility degradation. For these reasons, NO_x emissions from combustion processes are closely monitored and regulated.

During combustion NO_x is formed (95% as NO and 5% as NO_2) according to three different mechanisms and named differently after the mechanisms as thermal, prompt, and fuel NO_x. Thermal NO_x is formed when N_2 reacts with O_2 in the gas phase at temperatures higher than 1400 °C. The formation of thermal NO_x is highly temperature dependent. Prompt NO_x formation is involving the reaction of gaseous N_2 in the air and hydrocarbon free radicals. The formation of prompt NO_x is favoured in fuel-rich combustion regions, where the hydrocarbon free radicals are more likely available. Meanwhile, fuel NO_x is formed through physical and chemical transformations of nitrogen containing impurities of the fuel during combustion, which is virtually independent of the flame temperature at normal combustion conditions.

Depending on the combustion technology used and the combustion conditions, the formation and emission of NO_x can be controlled to a certain extent by the combustion process itself. In principle, for example, the formation of thermal NO_x can be reduced by operating the combustion at temperatures lower than 1400 °C and/or reducing the residence time at high temperatures. The formation of prompt NO_x can also be limited by reducing the flame temperature and/or increasing the air/fuel ratio. In the meantime, fuel NO_x formation can be reduced by combusting in local fuel-rich conditions and/or decreasing the concentration of fuel-bound nitrogen. Some of the most common preventive techniques for NO_x abatement of stationary sources by process control are represented in Table 1, including some end-of-pipe techniques for abatement of NO_x emission from combustion processes, which are well known as flue gas treatment technologies for NO_x reduction from stationary sources.

Selective catalytic reduction (SCR) of NO_x is a process in which NO_x is selectively reduced to nitrogen and water on a heterogeneous catalyst by a reducing agent such as ammonia (NH_3) in the presence of oxygen. Selective non-catalytic reduction (SNCR) of NO_x is a thermal De-NO_x process in which NO_x is converted into nitrogen and water by reacting with ammonia or urea ($H_2N–CO–NH_2$), normally injected into the upper part of the boiler or in the duct due to the fact that the optimum temperature for the conversion is within 870–1200 °C. The globally simplified reactions of SNCR are represented in Eqs. (1) and (2) [2].

$$2NO + H_2N-CO-NH_2 + 0.5O_2 \rightarrow 2N_2 + CO_2 + 2H_2O \tag{1}$$

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \tag{2}$$
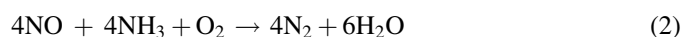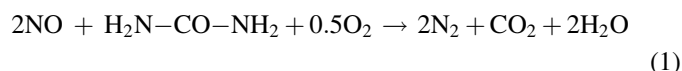
In practice, potential problems associated with this SNCR include incomplete mixing of ammonia with the hot flue gas and improper temperature control. If the temperature is too high, ammonia will be oxidized to NO_x, whereas unreacted ammonia will escape from the boiler if the temperature is too low. Ammonia is a corrosive gas being highly environmentally hazardous.

In addition, dry and wet sorption techniques have been reported for simultaneous removal of NO_x and SO_x ($SO_2 + SO_3$) from the flue gas. The wet technique employs a scrubbing system containing an aqueous solution of strong oxidizing agents such as $KMnO_4$ and $NaClO_2$ to convert insoluble NO into a form that can be removed by the scrubbing liquid [3]. An example of dry sorption technique, on the other hand, is to use copper oxide catalyst. Alumina supported copper oxide reacts with SO_x in the flue gas to form copper sulphate. Both copper oxide and copper sulphate are active in SCR of NO_x by NH_3 (NH_3-SCR) [4].

Among the end-of-pipe technologies available for abatement of NO_x in stationary sources, catalytic technique is one of the most widely and successfully used in industry [1,5]. It was estimated that one third of the US annual output of ammonia was used for SCR of NO_x in the US in the year 2000, and 50% of the thermal power plants in Japan is equipped with this technology [5]. However, the technology is quite costly, with potential risks of secondary environmental problems, such as NH_3 slip, associated with the use of ammonia. It has been reported that the applications of the conventional SCR technologies for control of NO_x (9 ppm) emission from stationary gas turbines cost 6.274, 3.541, and 1.938 USD per tonne for turbines with output median values of 5, 25, and

Table 1
Summary of characteristics and efficiencies of NO_x abatement techniques for stationary applications [1]

Technique	Principle	Efficiency (%)
Process control		
Water injection	Reduced peak temperature	40–70
Flue gas recirculation	Reduced combustion temperature	40–80
Reduced air preheat	Reduced peak temperature	25–65
Burner out of service	Reduced combustion temperature	30–60
Low-NO_x burners	Staged air and fuel	30–50
Flue gas treatment		
SCR	Chemical reduction of NO_x	70–90
SNCR	Chemical reduction of NO_x	25–50
Sorption	Chemical reduction of NO_x and absorption of SO_2	60–90

150 MW, respectively [5]. Therefore, it is worthwhile to promote research and development on high temperature catalysts for in-situ abatement of NO_x in stationary sources, particularly for small and medium applications.

2. Fluidized bed combustion and opportunities for in-situ catalytic abatement of NO_x

Fluidized bed combustion (FBC) is an advanced technology of high thermal efficiency and fuel flexibility for heat and power production from solid fuels. A distinguished feature of FBC is that the combustion takes place in a bed of solid particles, fluidized by means of air blown through the bed from below. The bed is composed of sand, fuel, ash, and additives for emission control. Due to the high heat capacity of the sand material and the relatively long residence time, the combustion can be completed at a relatively low temperature, typically of 800–900 °C, with a high thermal homogeneity throughout the bed. Consequently, the emission of NO_x from FBC is relatively low (100–300 ppm), and that of nitrous oxide (N_2O) is relatively high (50–150 ppm), compared to other combustion technologies. N_2O is a non-toxic gas but generally recognised as a greenhouse gas. It plays an important role in the depletion of ozone of higher layer of atmosphere and therefore also needs to be controlled.

During FBC, the nitrogen chemistry is extremely complicated with so many physical and chemical transformations. These transformations can take place homogeneously and heterogeneously, and the most important reactions are represented in Fig. 1 associated with Table 2.

Interestingly, while in industry additional NH_3 is injected into the flue gas downstream to support SCR of NO_x, ammonia occurs to be formed and available right in the combustion chamber during early stage (pyrolysis/devotilisation) of nitrogen transformation in FBC (Fig. 1). The formation of ammonia, as well as HCN, is indeed proved to be in agreement with the reality as shown in Fig. 2, which represents the axial concentration of NO_x precursors measured from an industrial
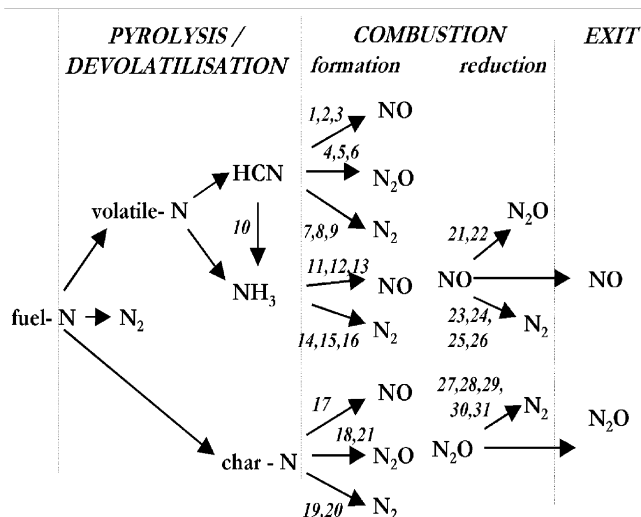
Table 2
Summary of the reactions presented in Fig. 1 [6]

#	Reaction	Homogeneous	Heterogeneous
1	$HCN \xrightarrow{+O,+OH} H_iNCO \xrightarrow{+H} NH_i \xrightarrow{+O_2,OH,+O} NO$	◆	–
2	$HCN \xrightarrow{+CaO,O_2} NO$	–	◆
3	$HCN \xrightarrow{+char,O_2} NO$	–	◆
4	$HCN \xrightarrow{+O} NCO \xrightarrow{NO} N_2O$	◆	–
5	$HCN \xrightarrow{+CaO,O_2,(NO)} N_2O$	–	◆
6	$HCN \xrightarrow{+char,O_2,(NO)} N_2O$	–	◆
7	$HCN \xrightarrow{+O,+OH} H_iNCO \xrightarrow{+H} NH_i \xrightarrow{+NO} N_2$	◆	–
8	$HCN \xrightarrow{+CaO,(O_2),NO} N_2$	–	◆
9	$HCN \xrightarrow{+char,(O_2),NO} N_2$	–	◆
10a	$HCN + O_2 + H_2 \xrightarrow{CaO} NH_3$	–	–
10b	$HCN \xrightarrow{+O_2,OH} H_iNCO \xrightarrow{+H} NH_i \xrightarrow{+H_2O,+H_2} NH_3$	◆	◆
11	$NH_3 \xrightarrow{+O,+OH} NH_i \xrightarrow{+O_2,+OH,+O} NO$	◆	–
12	$NH_3 \xrightarrow{+CaO,O_2} NO$	–	◆
13	$NH_3 \xrightarrow{+char,O_2} NO$	–	◆
14	$NH_3 \xrightarrow{+H,+OH} NH_i \xrightarrow{+NO} N_2$	◆	–
15	$NH_3 \xrightarrow{+CaO,(O_2),(NO)} N_2$	–	◆
16	$NH_3 \xrightarrow{+Char,(O_2),(NO)} N_2$	–	◆
17	$O_2 + (–C) + (–CN) \rightarrow (–CO) + (–CNO)$ $(–CNO) \rightarrow NO + (–C)$	–	◆ ◆
18	$O_2 + (–C) + (–CN) \rightarrow (–CO) + (–CNO)$ $(–CN) + (–CNO) \rightarrow N_2O + 2(–C)$	–	◆ ◆
19	$NO + (–C) \rightarrow 1/2N_2 + (–CO)$	–	◆
20	$N_2O + (–C) \rightarrow N_2 + (–CO)$	–	◆
21	$O_2 + (–C) + (–CN) \rightarrow (–CO) + (–CNO)$ $(–CNO) \rightarrow NO + (–C)$ $NO + (–CNO) \rightarrow N_2O + (–CO)$	–	◆ ◆ ◆
22	$2NO + CaSO_R \ (s) \rightarrow N_2O + CaSO_4 \ (s)$	–	◆
23	$NO + (–C) \rightarrow 1/2N_2 + (–CO)$	–	◆
24	$NO \xrightarrow{+char,+CO} N_2$	–	◆
25	$NO \xrightarrow{+CaO,+CO} N_2$	–	◆
26	$NO \xrightarrow{+CaO,H_2} N_2$	–	◆
27	$N_2O + H \rightarrow N_2 + OH$	◆	–
28	$N_2O + OH \rightarrow N_2 + HO_2$	◆	–
29	$N_2O + M \rightarrow N_2 + O + M$	◆	–
30	$N_2O + (–C) \rightarrow N_2 + (–CO)$	–	◆
31	$N_2O \xrightarrow{+CaO} N_2$	–	◆

FBC plant. A consideration of this formation and the additive application feature of the fluidized bed suggests a possibility for in-situ catalytic abatement of NO_x right in the combustion chamber by NH_3-SCR of NO_x with no need of NH_3 addition, and/or selective catalytic oxidation (SCO) of NH_3. Other possibilities are to take the opportunity of high temperatures to promote in-situ reduction of NO_x by catalytic decomposition of nitrogen containing gas species present in the combustion chamber, including NH_3, HCN, N_2O, and NO_x. The decomposition reactions usually have relatively high activation energies and therefore are thermodynamically favourable at high temperatures. These reactions, on the other hand, are not economical for the flue gas treatment downstream, due to the requirement of additional heating to overcome the high
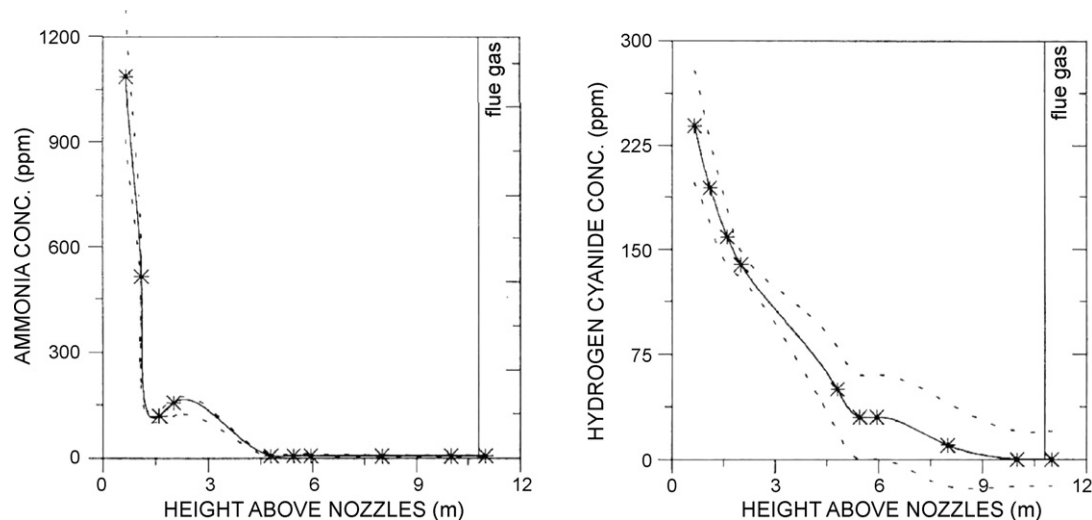

Fig. 1. Most important reactions of nitrogen transformation in FBC [6].

Fig. 2. Axial concentration of NO_x precursors in a 12 MWth FBC plant [8].

activation energies. The activation energy of NO decomposition reaction according to Reaction (3), for example, is as high as of 364 kJ/mol [7].

$$2NO \rightarrow N_2 + O_2 \qquad (3)$$

3. Challenges and catalysts for in-situ abatement of NO_x in FBC

3.1. Challenges for in-situ catalytic abatement of NO_x in FBC

As discussed earlier, a disadvantage of FBC compared to other combustion technologies is its relatively high emission of N_2O. This disadvantage can be minimized by applying the approach of in-situ catalytic abatement of NO_x including removal of NH_3 and/or HCN, as NH_3 and HCN are precursors of both NO_x and N_2O in FBC. Taking this into account with a consideration of the cost and potential secondary environmental problems of the conventional SCR of NO_x, as well as the huge amount of NH_3 consumed annually for this technology, it is reasonable to believe that in-situ catalytic abatement of NO_x in FBC would be economically and environmentally favourable. However, the question is whether or not there exist catalysts capable of doing the job in the hostile environment of FBC with:

- high temperatures (800–900 °C),
- high concentrations of water vapour and dust,
- high risks of poisoning by SO_2 and vapours of volatile metals, and
- alternating oxidizing and reducing atmospheres.

Among these, the challenge associated with high temperatures is most critical, because of the temperature limitations of contemporary catalysts for NO_x abatement. Indeed, there exist today so many types of heterogeneous catalysts commercially available and capable of reducing effectively NO_x emission from the industrial processes including combustion. These catalysts can be generally grouped in three major families of noble metals, metal oxides, and zeolites, with some overlapping in between. For example, noble metals are commonly supported by zeolites, and metal oxides can be doped with noble metals in order to improve the catalyst performance. The working temperature windows of these three catalyst families are shown in Fig. 3. Unfortunately, these windows are not in line with the temperature range of 800–900 °C encountered in FBC. The term "high temperature SCR" used in the literature and industry is just referred to the SCR technology that can operate from 400 °C to the upper limit of 600 °C [5]. It is therefore important to identify possibilities for the development of a solid material with a high catalytic activity for in-situ abatement of NO_x at FBC temperatures.

3.2. Catalytic processes and materials for NO_x abatement at high temperatures

Another way of classifying catalysts is to look at the catalytic reactions. Apart from SCR by NH_3 and NO_x emission from FBC can be catalytically reduced by different processes, which include chemical decomposition, SCR of NO_x by
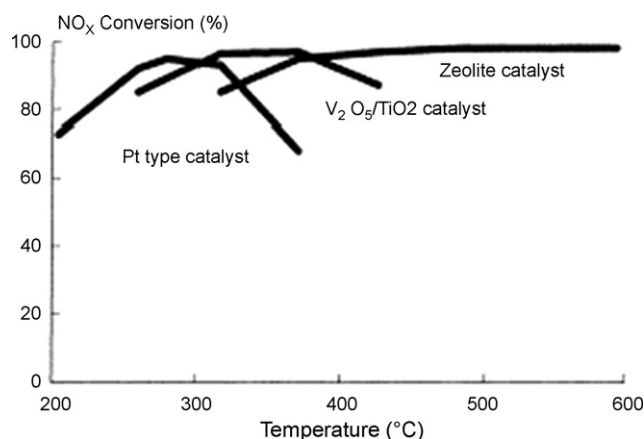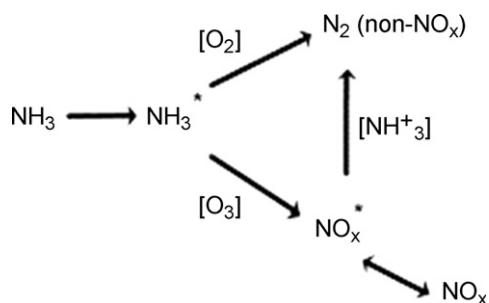

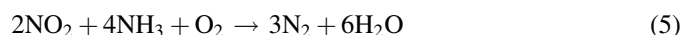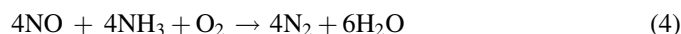Fig. 3. Temperature limitations of SCR-NO_x catalysts [9].

Fig. 4. Reaction scheme for NH$_3$-SCR of NO$_x$ [9].

hydrocarbons (HC-SCR), non-selective catalytic reduction (NSCR) or three ways catalyst (TWC), and SCO of ammonia, which will be discussed below with the focus on their capability to operate effectively at FBC temperatures.

3.2.1. NH$_3$-SCR of NO$_x$

In the process of selective catalytic reduction of NO$_x$ by NH$_3$ several reactions are known to occur but it is best represented by Reactions from (4) to (7) and the reaction scheme depicted in Fig. 4

Selective reactions

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad (4)$$

$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O \qquad (5)$$

Non-selective reactions

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad (6)$$

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \qquad (7)$$

Basically, NH$_3$ can react selectively with NO$_x$ to form N$_2$, according to Reactions (4) and (5), or react non-selectively to produce NO$_x$ or N$_2$. This parallel reaction scheme gives rise to the temperature dependent performance curve, shown in Fig. 5, typically characteristic for NH$_3$-SCR of NO$_x$. This indicates that the inherent non-selective ammonia oxidation reaction to form NO, Reaction (6), is favoured at the higher temperature area of the temperature window and is directly responsible for the temperature limitation in the performance of NH$_3$-SCR catalysts.
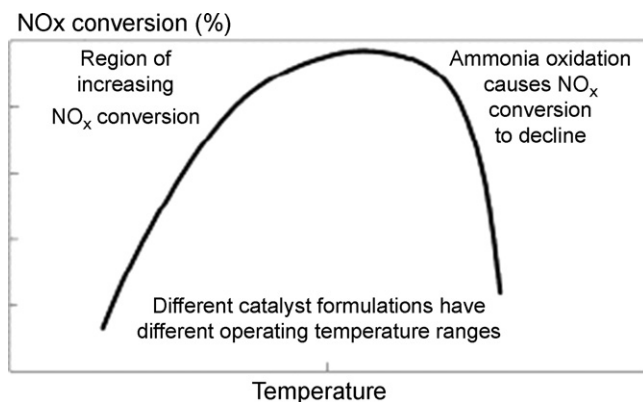
Fig. 5. Maximum performance for NH$_3$-SCR of NO$_x$ [9].

Many materials have been studied as catalyst for NH$_3$-SCR of NO$_x$, including noble metals, metal oxides, and zeolites. Up to now, no catalyst of this type has been reported to be active at temperatures higher than 600 °C, which is by far lower than FBC temperatures.

3.2.2. HC-SCR of NO$_x$

SCR of NO$_x$ can also be promoted by hydrocarbon (HC) as reducing agent in the presence or even excess of oxygen. In a NO$_x$–C$_n$H$_m$–O$_2$ system, several reactions may occur [10], including

(a) decomposition of NO to N$_2$ and O$_2$,
(b) oxidation of NO by oxygen to NO$_2$,
(c) reduction of NO by the HCs to N$_2$O and N$_2$, and
(d) oxidation of the hydrocarbons by oxygen to CO/CO$_2$.

Generally, the composition and concentration of HCs have significant influence on NO$_x$ reduction efficiency [11,12]. Increased HC concentration tends to increase NO$_x$ reduction efficiency while shifting the maximum NO$_x$ conversion point towards slightly higher temperatures. The activity of individual C$_1$–C$_4$ HCs towards HC-SCR of NO increase with increasing number of carbon atoms in the HC molecule, and the alkenes are more active in this process than the alkanes.
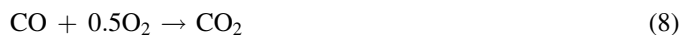
Supported noble metals have been proved very active in HC-SCR of NO$_x$, but within very narrow temperatures windows. The efficiency HC-SCR of NO$_x$ is only slightly affected by the presence of water, but it is quite sensitive to sulphur dioxide poisoning. Another problem associated with supported noble metals catalysts is the formation of nitrous oxide [13].

Compared to noble metals, metals oxides exhibit moderate activities, but the operation temperatures are higher. The activities are however strongly subjected to deactivation by sulphur dioxide and to thermal ageing due to loss of specific area [13]. Zeolites, on the other hand, are active towards HC-SCR of NO$_x$ at relatively high temperatures and promoted by the presence of oxygen. But the problem is that the catalysts are subject to hydrothermal deactivation as well. More importantly, at temperatures higher than 500 °C, all of the HCs are consumed by the combustion reactions with oxygen [13]. Farrauto and Heck [14] have concluded that research for active and stable catalysts, which would utilize onboard HCs as reducing agents, has not been successful and likelihood of success in the future is low.
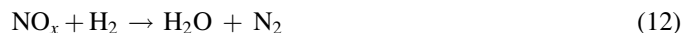
3.2.3. NSCR of NO$_x$

NSCR of NO$_x$ for stationary applications is actually derived from TWC of automotive catalysis. The basic chemical reactions occur in oxygen-rich atmospheres of as follows:

Deplete of oxygen

$$CO + 0.5O_2 \rightarrow CO_2 \qquad (8)$$

$$H_2 + 0.5O_2 \rightarrow H_2O \qquad (9)$$

$$HC + O_2 \rightarrow CO_2 + H_2O \qquad (10)$$

Convert NO_x

$$NO_x + CO \rightarrow CO_2 + N_2 \tag{11}$$

$$NO_x + H_2 \rightarrow H_2O + N_2 \tag{12}$$

$$NO_x + HC \rightarrow CO_2 + H_2O + N_2 \tag{13}$$

Under suitable conditions, TWC containing noble metals (Pt, Rh, or Pd) can simultaneously reduce more than 95% of CO, HC, and NO_x in exhaust gas, and are extensively used for controlling automotive emissions [15]. There are two major problems associated with the use of TWC. First, in lean combustion conditions, TWCs are not effective in reducing nitrogen oxides. This problem however can be solved by adding an alkali earth element such as BaO to the catalysis system for NO_x storage during lean conditions. Secondly, the conversion efficiency of the catalysts is high only when the combustion is operated within a narrow band of air/fuel ratios very close to the stoichiometric value. Thus, it is required to maintain sufficiently accurate control of the mixture ratio, which is not practical for FBC applications.

3.2.4. Catalytic decomposition of NO_x

Most of the past studies on catalytic decomposition of NO_x focused on NO, perhaps due to the fact that 95% of NO_x from combustion is NO. The global reaction for decomposition of NO on heterogeneous catalysts is represented in Eq. (3) above, of which the activation energy is 364 kJ/mol. It is generally agreed that the decomposition of NO involves the dissociation of NO to nitrogen and oxygen on a catalytic surface and that nitrogen readily desorbs as N_2 while oxygen is strongly retained on the surface. Because desorption of oxygen from the surface is the rate-limiting step, the overall, decomposition is inhibited by the presence of oxygen. However, it should be noted from solid state and kinetic point of view that the oxygen desorption is strongly temperature dependant and would increase with increasing temperature. Therefore, NO catalytic decomposition should be favourable at high temperatures with regards to the oxygen inhibition effect.

Several catalysts including zeolites, metal oxides, and noble metals have been reported in the literature to exhibit catalytic activity towards NO decomposition reaction [13]. Among the tested zeolites based catalysts, Cu-ZSM-5 is the most active catalyst at low temperatures with a maximum activity at around 500 °C [13,16]. At higher temperatures, however, the activity of Cu-ZSM-5 decreases due to an increasing desorption of NO.

Metal oxides such as Cr, Fe, Co, and Ni are also active catalysts for NO decomposition [13], for which the common difficulty posed by the slow desorption step of oxygen can be reduced by reasonable choice of promoter. For example, Hamada et al. [17] have demonstrated that, by adding silver to cobalt oxide, both activity and resistance to oxygen inhibition are increased. Perovskite types of metal oxides have attracted much interest of investigation for applications in NO decomposition, due to their thermal stability and the finding that defective perovskites permit easy desorption of a large amount of oxygen from the surface, thereby promoting the overall decomposition process of NO [13]. Several perovskites including manganites,

cobaltites, and ferrites, as well as $YBa_2Cu_3O_{7-x}$ and La_2CuO_4, have been reported to exhibit good performance for the decomposition of NO at temperatures above 750 K and are quite stable for long-term operation at these high temperatures [18–24]. However, the fact that perovskites have low surface area and inferior catalytic properties limit their practical applications. In addition, these catalysts are not suitable to disperse on alumina for the surface area enhancement due to the relatively large particle size of perovskites and their reactivity with alumina [25].

Noble metals are generally active for NO decomposition at higher temperatures than zeolites and metal oxides [26]. The majority of NO decomposition studies for noble metals have been carried out upon either Pt alone or its alloys [13]. Pt–Al_2O_3, for example, exhibited good initial decomposition activity at 973 K. However, its activity decayed quickly with time [26]. In the meantime, palladium generally displays a similar catalytic activity as platinum but has a better thermal stability. It has been reported that Pd–Al_2O_3 catalysts were quite active with a long life time in NO decomposition and showed a high resistance against the inhibition of oxygen and SO_2 at temperatures higher than 1100 K [26]. Furthermore, the addition of a small amount of gold or silver significantly enhanced the catalytic activity of Pd–Al_2O_3 (Fig. 6).

3.2.5. SCO of NH_3

Apart from De-NO_x technologies, it is alternatively possible to reduce NO_x emission from combustion by means of SCO of NH_3, a precursor of NO_x in combustion process. In the presence of oxygen, the following reactions may take place on the catalysts:

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \tag{14}$$

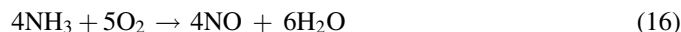$$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O \tag{15}$$
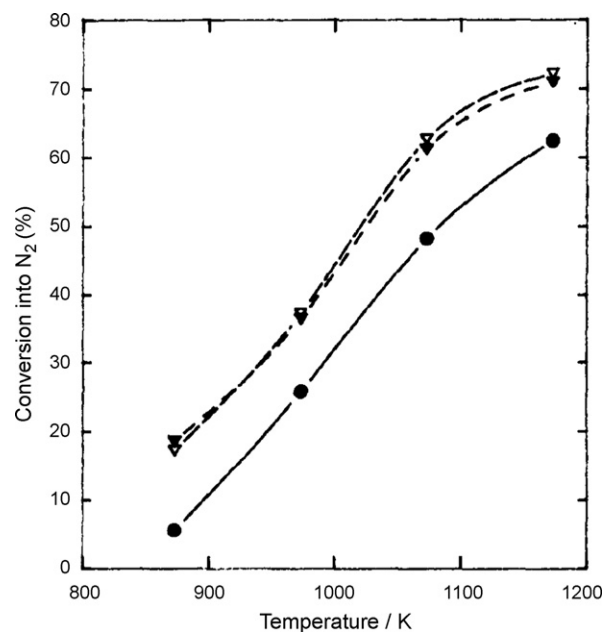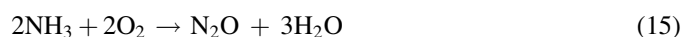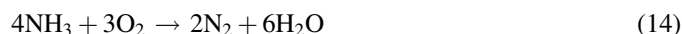
Fig. 6. N_2 conversion for NO decomposition over Pd/Al_2O_3, Pd–Au/Al_2O_3 and Pd–Ag/Al_2O_3 catalysts. (▽) 0.5% Pd-0.03% Au/Al_2O_3, (▼) 0.5% Pd-0.06% Ag/Al_2O_3 and (●) 0.5% Pd/Al_2O_3 [26].

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad (16)$$

Various types of materials have been studied as catalysts for SCO of ammonia. Noble metals including Pt, Rh, Pd, Ru, Ir, and Ag have been found to be very active catalysts for ammonia oxidation [27–31]. The next group of the studied catalysts for the ammonia SCO process is based on zeolites. Zeolites modified with transition metals have been found to be promising catalysts for SCO of ammonia. Long and Yang showed a high activity of copper and iron deposited on the ZSM-5 [32] and Y-zeolites [33]. A decrease in Si/Al ratio improves the catalytic activity of zeolites. An additional increase in the activity of the Fe-modified zeolites can be obtained by the deposition of noble metals (Pt, Pd, and Rh) [27]. However, the working temperature windows reported were by far lower than the temperatures encountered in FBC.

Research on SCO of NH_3 using catalysts containing transition metal oxides such as MnO_2, Co_3O_4, Fe_2O_3, CuO, MoO_3, or V_2O_5 has been quite active during the last decade [34–41]. In general, these catalysts show higher selectivity to nitrogen and operate at temperatures significantly higher than that of two first groups. Particularly, metal mixed oxides obtained by calcinations of hydrotalcite-type (HT) compounds have been found very active for SCO of ammonia. Most notably, Chmielarz et al. [34] have performed a thorough investigation of SCO of ammonia on HT mixed oxides containing Cu, CO, Fe, or Ni. In this study, the catalytic activity was measured at temperatures ranging from 50 to 650 °C, but the TPR (temperature-programmed reduction) of the samples was carried out in the temperature range of 80–950 °C. They reported that the highest activity of 100% was observed for copper containing samples, followed by those of Co, Ni, and Fe. This order of activity is opposite to that found for the selectivity towards N_2 with the exception of copper (Fe > Ni > Cu > Co). In addition, an increase in Cu loading only slightly influences the activity, but resulted in a decrease of the selectivity to nitrogen and an increase of the selectivity to NO (Fig. 7). The highest catalytic activity and N_2 selectivity was measured for the catalyst with lowest transition metals, within the investigated range. More notably, the reaction temperature was reported to be a very important factor affecting the selectivity of ammonia oxidation products. N_2 is a dominant reaction product in the lower temperatures, while at higher temperatures the selectivity to NO increases. However, at higher temperatures, NO formed by SCO of NH_3 is reduced by unreacted NH_3, which is confirmed by De-NO_x experiments performed on the same catalysts. Overall, in the best case of the copper containing samples (5 mol% copper catalyst, Fig. 7A), at 650 °C, the NO selectivity is still as low as about 13% and that of N_2 is as high as about 80%.

3.2.6. Summarising discussion

At this point, it is reasonable to believe that the idea to develop a low-NO_x bed material for FBC is technically feasible. While there are still uncertainties in the literature with regards to the selectivity of SCO catalysts effective at temperatures close to FBC temperatures, the catalytic decomposition of NO on supported noble metals like Pd–Al_2O_3 system, for example, has proved practically effective at FBC temperatures. In addition, the catalytic decomposition of other nitrogen containing combustion gas species such as NH_3 and N_2O on solid materials such as bauxite, quartz sand, dolomite, limestone, and other bed materials has also been reported to be significantly active at FBC conditions [42–48]. Perovskite types of metal oxides, despite of their low surface area and inferior catalytic properties, are still worthwhile to be investigated for the development, due to their high thermal stability. At FBC temperatures, they may become more active towards catalytic reactions for NO_x abatement. Perovskites of Cu and Ba, like $YBa_2Cu_3O_{7-x}$ for example, are good candidates for this study option. More promising materials of the metal oxide catalyst group for the development are HTs. Metal oxides such as Cu and Fe obtained from calcinations of HTs have proved not only to promote effectively SCO of NH_3, but also SCR of NO at temperatures close to FBC temperature [34].

Application of zeolites to this development seems less likely to success due to their thermal catalytic deactivation. The thermal catalytic deactivation of Cu-ZSM-5, one of the most actively studied and widely used De-NO_x catalysts, has been studied at temperatures ranging from 100 to 600 °C by Tanabe et al. [49]. The catalyst tests were carried out in consistent conditions on the Cu-ZSM-5 samples differed from one another by subjecting to different thermal pre-treatment in different temperatures up to 800 °C for the equal time period of 5 h. It is
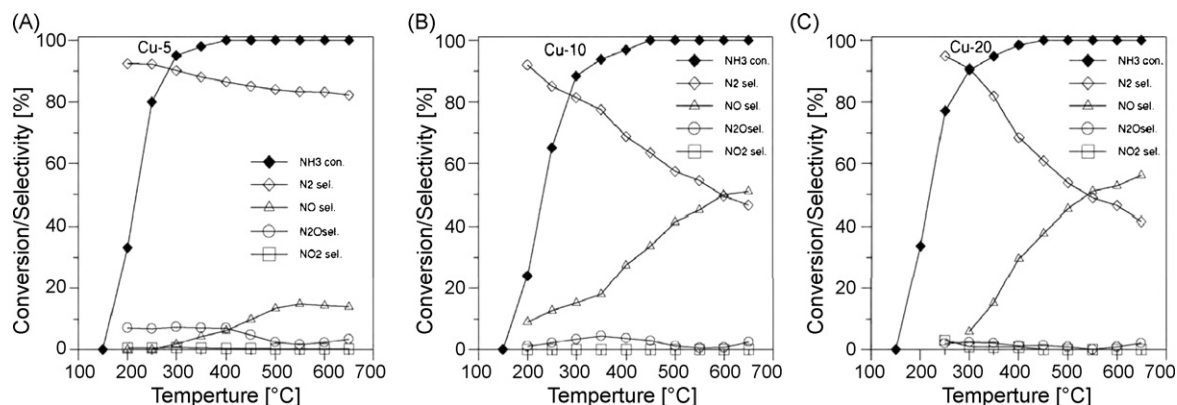

Fig. 7. SCO of ammonia by copper containing HT catalysts [34].

reported that the higher pre-treatment temperatures, the less active catalysts. The deactivation is as much as 80% by comparing between unheated sample and the sample being preheated at 800 °C for 5 h. Nevertheless, there is no general agreement on the cause of the deactivation, especially with regards to the catalyst structure such as de-alumination or sintering [13]. Therefore, it would still be worth to investigate the use of zeolite based catalysts, mainly Cu and Fe zeolites, for the development under consideration.

4. Ash based catalytic materials for in-situ abatement of NO$_x$ in FBC

4.1. Activity of ash towards catalytic abatement of NO$_x$ in FBC conditions

A promising option for the development of a low-NO$_x$ catalyst is to utilize ash from FBC itself. This idea is triggered from reviewing recent studies in catalytic reduction of NO$_x$ on bed materials from FBC plants. It has been reported that FBC bed materials were active towards catalytic reduction of NO by CO at FBC temperatures [50–54]. In addition, the catalytic activity was found to be directly proportional to the amount of Fe$_2$O$_3$, Al$_2$O$_3$, MgO, and CaO on the bed particles [53,54], which are the main components of solid fuel combustion ashes as represented in Table 3.

In the meantime, Zhaopin and Jixiang [55] studied the effects of ash recycling and direct ammonia injection on NO$_x$ emission from an FBC test facility. They found that the more fly ash was recycled, the less NO$_x$ was emitted from the test facility within the range of 0–2.5 as the fly ash recycle ratio (Rq) at the bed temperature of 880 °C (Fig. 8). In addition, the reaction of selective reduction of NO by NH$_3$ was found to be very effective at temperatures lower than 910 °C. Above this temperature, the homogeneous reaction of NO formation from NH$_3$ became predominant, giving rise to an increase in the overall NO$_x$ emission from the test. Although it was not clearly presented, the positive effect on selective reduction of NO by NH$_3$ was presumably due to the catalytic effect of the fly ash recycled, considering the highest ratio of fly ash recycle (Rq = 2.5) within the range used for the experiments [55].
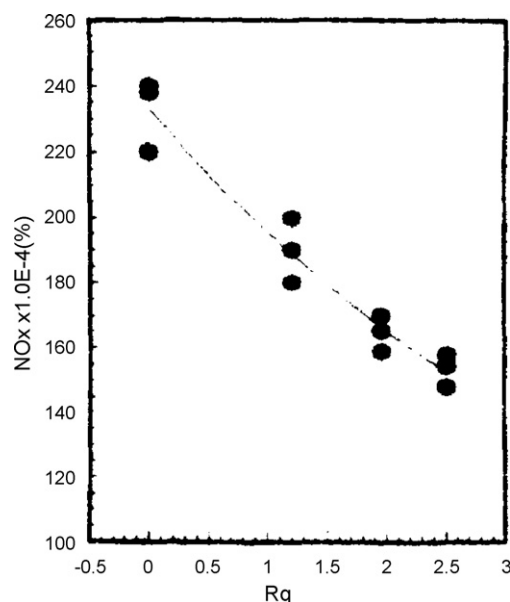

Fig. 8. The effect of fly ash recycle ratio (Rq) on NO$_x$ emission from an FBC test facility [55].

4.2. Utilization of fly ash for development of low-NO$_x$ bed materials

Combustion fly ash has a number of properties suitable for use as heterogeneous catalyst or catalyst carrier for high temperature gas cleaning [56,57]. Indeed, fly ash is composed of very fine and porous particles. For coal fly ash for example, the ash particle size is ranging from 10 to 100 μm, while the surface area is varied within the range of 0.9–16.5 m^2/cm^3 [58]. Some fly ash fractions, particularly those of fly ash from municipal solid waste (MSW) combustion, are enriched with transition metals such as Cu, Cr, Co, and Ni, which are commonly used for NO$_x$ reduction catalysts. These properties and the catalytic activity towards reduction of NO$_x$ at FBC conditions of fly ash make it a promising candidate as starting material to develop a low-NO$_x$ bed material for FBC, especially bubbling FBC in which by the concept the ash is not recycled.

For the simplest applications, fly ash may just be pelletized to produce solid particles within a size range suitable for use in FBC and tested for the catalytic activity. Moreover, the surface of fly ash can be further treated and modified in order to obtain bed materials with higher catalytic activity for nitrogen containing gas species reduction and high resistance to the hostile environments in FBC plants. For example, the fly ash surface can be modified by tailoring with suitable catalysts including De-NO$_x$ catalysts and catalysts for abatement of NO$_x$ precursors at high temperatures, which have been discussed earlier in this study. It is however important that the catalytic materials to be obtained will be inexpensive, being viable for FBC plants. Therefore, to utilize process waste streams, which may contain metals of interest, would be a good complimentary option to promote the development in this direction, making it economically feasible. Orlik [10] reported relevant developments including a patent, Ukrainian Patent No. 32552, which

Table 3
Ash composition of different solid fuels [48]

Ash composition (wt% of ash)	Coal	Wood pellets	Bark	Peat	Sludge
SiO$_2$	52.09	12.84	17.58	43.41	27.43
Al$_2$O$_3$	21.36	2.36	3.78	10.13	14.53
Fe$_2$O$_3$	6.46	1.68	2.6	7.67	22.3
CaO	5.72	32.53	34.48	12.17	5.68
MgO	2.02	5.39	3.91	2.14	1.24
P$_2$O$_5$	0.84	2.81	3.76	5.98	15.67
Na$_2$O	0.21	0.71	0.19	0.37	0.14
K$_2$O	2.3	12.95	7.31	2.27	1.65
SO$_3$	6.3	3.81	3.39	6.51	4.96
Cl$^-$	0.08	1	0.46	0.58	0.1
CO$_2$	6.38	24	10.48	4.25	3.92
Sum	103.76	100.08	87.94	95.48	97.62

allow using, spent solutions from electrochemical processes to produce catalysts for SCR of NO_x by NH_3.

4.3. Zeolites from fly ash

Due to the compositional similarity of fly ash to volcanic materials related precursors of natural zeolites, as well as the increasingly stringent legislations on ash disposal, much interest has been attracted to the study of zeolite synthesis from fly ash [59–69]. Many methods have been proposed for synthesizing of zeolites from fly ash, but they are all primarily based on the hydrothermal alkaline conversion of fly ash. Typically, the process consists of three major steps: fusion of caustic soda and fly ash for optimal extraction of silicate and aluminate, aging step which provides time for formation of nuclei, and hydrothermal crystallization resulting in activation of nuclei into well defined crystals [61]. By varying the experimental conditions, Steenbruggen and Hollman [66] produced different types of zeolites such as zeolite Na-P1, zeolite K-G and, zeolite ZK19. They also performed sorption experiments in aqueous solutions of different metals and found that the selectivity series for zeolite Na-P1 is $Ba > Cu > Cd \approx Zn > Co > Ni$. The sorption selectivity properties of ash derived zeolites towards different metals in aqueous solutions would facilitate the utilization of spent solutions from electrochemical industry for low cost production of zeolites supported metals or metal oxides catalysts. Using different processes for synthesis of low-silica sodium and potassium zeolites from fly ash Querol et al. [60], on the other hand, have found that the resulted high A1(III)/Si(IV) ratio zeolites account for a high ion exchange potential, especially for ammonium and heavy metals, which may have significant application in De-NO_x technology.

5. Concluding remarks

Opportunities, challenges, and possibilities to develop a bed material for in-situ catalytic abatement of NO_x in FBC, especially bubbling FBC plants of small and medium sizes, have been identified. The idea of developing such a low-NO_x bed material appears to be technically feasible. In addition, such a development would be economically and environmentally favourable, considering the cost and potential environmental problems associated with the use of NH_3 for the conventional NH_3-SCR of NO_x, as well as the huge amount of NH_3 annually used for this purpose worldwide. In addition, in-situ catalytic removal of NH_3 and/or HCN would limit the emission of N_2O, a greenhouse gas, into the atmosphere as well, since they are precursors of both NO_x and N_2O emitted from FBC.

Direct fly ash utilization for the development appears to be a promising option of high feasibility. On the other hand, surface and structure modifications of fly ash for the development are also possible. Overall, the following materials are of interest for experimental investigation of the development:

- fly ash subjected to thermal and/or chemical treatments,
- zeolites including zeolites from fly ash,
- Pd–Al_2O_3, and
- hydrotalcite and perovskite type oxides of Cu, Fe, Co, Ni, Ba, and Pd.

Last but not least, to utilize of spent solutions from electrochemical industry for catalyst production is also an opportunity to reduce the catalyst cost and negative environmental impacts of this industry. This should be integrated to all of the options above, if and when possible.

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